# THIAZOLOPYRIDINIUM SALTS WITH AN ACTIVE METHYL GROUP AND CYANINE DYES BASED ON THEM

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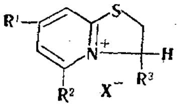
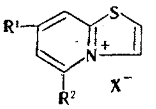
5-Methyl- and 7-methylthiazolo[3,2-*a*]pyridinium salts were synthesized. Condensations leading to the formation of cyanine dyes were carried out at the active methyl groups of these salts.

Thiazolino[3,2-*a*]pyridinium salts (I) were described in [1], and styryls and monomethylidynecyanines were obtained from them.



I



II

I a $R^1=H$, $R^2=CH_3$, $R^3=OH$; b $R^1=H$, $R^2=CH_3$, $R^3=OC_2H_5$; c $R^1=CH_3$, $R^2=H$, $R^3=OH$; d $R^1=CH_3$, $R^2=H$, $R^3=OC_2H_5$; X=Br, $ClO_4$; II a $R^1=H$, $R^2=CH_3$, b $R^1=CH_3$, $R^2=H$

In the present research we have investigated the conversion of salts Ia-d with the loss of a water (or alcohol) molecule to thiazolopyridinium salts II; we also compared the colors of dyes of the same type from I and II.

The conversion to salt II was carried out both by [2] prolonged heating of salts I with 48% hydrobromic acid and by [3] the action of sulfuric acid in the cold. The yields for the 5-methylthiazolino[3,2-*a*]pyridinium salt were 40 and 54%, while the yields for the 7-methyl isomer were 55 and 72%, respectively. Salts II were identified in the form of the stable perchlorates. Their UV spectra are extremely simple and are characterized by two maxima at 227-230 and 306-315 nm for the 5- and 7-methyl isomers, respectively.

Salts II with a 7-methyl group proved to be more reactive than their 5-isomers. Dyes were obtained from them by the usual method (null-methylidynemerocyanines and styryls) and by an original method — by treatment with sulfuric acid of dyes with thiazolinopyridinium rings (styryls).

Unfortunately, the most suitable subjects for a comparison of the colors of the dyes — symmetrical carbocyanines — could not be obtained.

The optical characteristics of the new dyes (III-VIII), of which V and VI were previously synthesized [1] and are taken for comparison, are presented in Table 1. It is clearly seen that a hypsochromic shift of the absorption maximum is observed on passing from styryls from salts I (dyes V and VI) to styryls from salts II (dyes III and IV). The explanation for this can be found in an examination of limiting structures III-III' and V'V'. Structure V', which is characteristic for the excited state, is less

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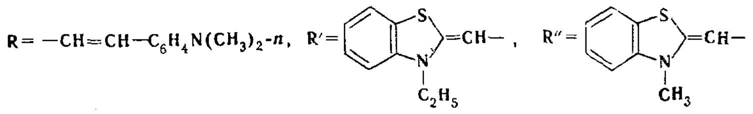
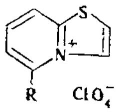
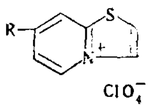
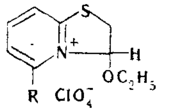
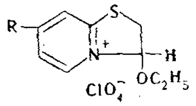
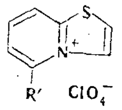
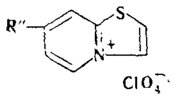
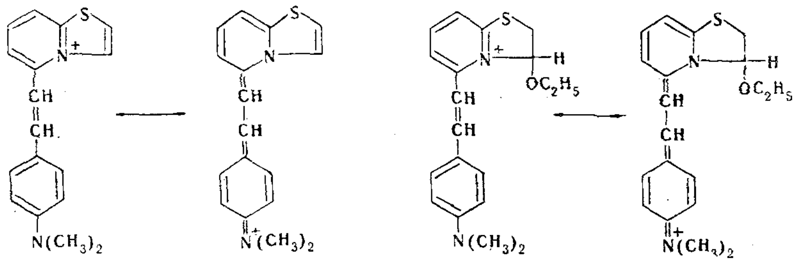
Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. T. G. Shevchenko Kiev State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1335-1337, October, 1974. Original article submitted November 5, 1973.

TABLE 1. Monomethylidynecyanines and Styryls with Thiazolopyridinium Rings



| Compound | Formula | $\lambda_{max}$, nm | log ε |
|---|---|---|---|
| III |  | 462 | 4,46 |
| IV |  | 476 | 4,68 |
| V |  | 480 | 4,47 |
| VI |  | 490 | 4,20 |
| VII |  | 472 | 4,95 |
| VIII |  | 470 | 4,98 |

favorable than V, inasmuch as the aromaticity of two rings — pyridine and benzene — is lost in this case. In the III-III′ structures the second is still less favorable as a consequence of loss of aromaticity in three rings. Thus the difference in the energy states of V-V′ is less than in the case of III-III′; transition to the excited state for salt III requires greater energy, and this induces a hypsochromic shift of its absorption band as compared with V.



III III′ V V′

The negative inductive effect of the ethoxy group may play a certain role in the deeper color of salt V, inasmuch as delocalization of the electrons of the chromophore leading to a bathochromic effect increases as the basicity of the heterocyclic rings of the styryls decreases. The same rationale is also applicable to the second pair of comparable styryls (VI and IV).

Styryls with p-dimethylamino groups in the para position relative to the bridge-nitrogen atom of the condensed system absorb in the longer-wave portion of the spectrum than their ortho isomers, as one should have expected.

## EXPERIMENTAL

5-Methylthiazolo[3,2-*a*]pyridinium Perchlorate (IIa). A) A 0.55-g (2 mmole) sample of 3-ethoxy-5-methylthiazolino[3,2-*a*]pyridinium bromide was dissolved in 10 ml of 48% HBr, and the mixture was refluxed for 60 h. The acid was then removed by vacuum distillation, and the yellow semisolid residue was dissolved in the minimum amount of water, after which 0.24 g (2 mmole) of sodium perchlorate was added. Workup gave 0.18 g (40%) of a product with mp 188-189° (from alcohol). Found: Cl 14.3; S 13.0%. $C_8H_8ClNO_4S$. Calculated: Cl 14.2; S 12.8%.

B) A 0.55-g sample of 3-ethoxy-5-methylthiazolino[3,2-*a*]pyridinium bromide was dissolved in 1 ml of concentrated $H_2SO_4$, after which the solution was allowed to stand for 24 h. It was then neutralized with sodium carbonate solution and extracted with chloroform. The solvent was removed by distillation, and the residue was worked up as described in method A to give 0.24 g (53%) of a product with mp 188-189°.

7-Methylthiazolo[3,2-*a*]pyridinium Perchlorate (IIb). This compound [0.25 g (55%)], with mp 86-87° (from isopropyl alcohol), was obtained from 0.55 g (2 mmole) of 7-methyl-3-ethoxythiazolino[3,2-*a*]pyridinium bromide by method A. Method B yielded 0.36 g (72%) of the same product. Found: Cl 14.4%. $C_8H_8ClNO_4S$. Calculated: Cl 14.2%.

5-(p-Dimethylaminostyryl)thiazolo[3,2-*a*]pyridinium Perchlorate (III). A) A 0.21-g (0.5 mmole) sample of 3-ethoxy-5-(p-dimethylaminostyryl)thiazolino[3,2-*a*]pyridinium perchlorate was dissolved in 1 ml of concentrated $H_2SO_4$, and the mixture was allowed to stand for 36 h. It was then neutralized with sodium carbonate and extracted with chloroform. The solvent was removed by distillation to give 0.092 g (48%) of a product that did not melt up to 300° (from methanol). Found: S 8.6%. $C_{17}H_{17}ClN_2O_4S$. Calculated: S 8.4%.

B) A 0.24-g (1 mmole) sample of 5-methylthiazolo[3,2-*a*]pyridinium perchlorate was dissolved by heating in 15 ml of absolute ethanol, after which 1 mmole of p-dimethylaminobenzaldehyde and 0.1 g (1 mmole) of piperidine were added, and the mixture was refluxed for 5 h. The dye precipitated. Workup gave 0.17 g (44%) of product.

7-(p-Dimethylaminostyryl)thiazolo[3,2-*a*]pyridinium Perchlorate (IV). A) This compound was obtained as in the preceding experiment from 3-ethoxy-7-(p-dimethylaminostyryl)thiazolino[3,2-*a*]pyridinium perchlorate after the sulfuric acid solution had stood for 24 h. The yield of product with mp 283-285° (from methanol) was 0.11 g (57%). Found: S 8.4%. $C_{17}H_{17}ClN_2O_4S$. Calculated: S 8.4%.

B) The dye was obtained in alcohol with piperidine from 7-methylthiazolo[3,2- ]pyridinium perchlorate. The yield of product with mp 283-284° was 0.2 g (52%).

5-(3-Ethylbenzothiazolin-2-ylidenemethylene)thiazolo[3,2-*a*]pyridinium Perchlorate (VII). A 0.24-g (1 mmole) sample of 5-methylthiazolo[3,2-*a*]pyridinium perchlorate was mixed with 2 ml of acetic anhydride, and 0.24 g (1 mmole) of 1-ethylbenzothiazole-2-sulfobetaine and 1 mmole of triethylamine were added. The mixture was heated for 20 min, during which the dye precipitated. The yield of product with mp 233° (from methanol) was 0.12 g (29%). Found: S 15.6%. $C_{17}H_{15}ClN_2O_4S_2$. Calculated: S 15.6%.

7-(3-Methylbenzothiazolin-2-ylidenemethylene)thiazolo[3,2-*a*]pyridinium Perchlorate (VIII). This compound was obtained by the preceding method from 7-methylthiazolo[3,2-*a*]pyridinium perchlorate in 4 ml of acetic anhydride. The yield of product with mp 258-259° was 0.14 g (36%). Found: S 16.1%. $C_{16}H_{13}ClN_2O_4S_2$. Calculated: S 16.1%.

## LITERATURE CITED

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